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(54) Method for preparing 4,4'-biphenol.

(57) 4,4'-Biphenol is prepared through debutylation of 3,3',5,5'-tetra-tert-butyl-4,4'-biphenol in an organic solvent in the presence of an acid catalyst wherein the debutylation is carried out continuously using at least two reactors aligned in series, with a high yield and high purity on an industrial level.

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BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a method for preparing 4,4'-biphenol. More particularly, the present invention relates to an economical method for preparing 4,4'-biphenol with high purity.

4,4'-Biphenol of the desired product to be prepared by the method of the present invention has recently been attracting a great deal of attention as a starting material for heat-resistant engineering plastics and the like. With the method of the present invention 4,4'-biphenol with enough purity for use as a raw material for these plastics can be prepared economically.

Description of the Background Art:

4,4'-biphenol (referred to as BPL hereinafter) has been prepared by the following methods: alkali fusion of diphenyl disulfonic acid; hydrolysis of dibromodiphenyl; oxidative dimerization of 2,6-ditert-butyl phenol (referred to as 2,6-DTBP hereinafter) to 3,3',5,5'-tetra-tert-butyl biphenol (referred to as TBBPL hereinafter) and subsequent debutylation thereof; and the like. In the former two methods severe reaction conditions are required and separation of large amounts of inorganic salts used in these reactions from the products is difficult, and therefore the oxidative dimerization of 2,6-DTBP is most preferably used to prepare BPL on an industrial level.

However, the process to produce BPL through the 2,6-DTBP route has not yet been fully economical or effective, particularly because the debutylation reaction has been proceeded in a batch process. The major problem of the debutylation reaction is the large endothermic reaction which requires large amounts of heat input to proceed with the reaction.

Consequently, the batch reactor requires a large of heat supply capacity to get high yields and quality of BPL. On the other hand, continuous processes using one reactor, which have never been known to give high yields with good quality, require very severe conditions, such as high temperatures, long detention time, and high concentrations of catalysts, which cause low selectivity and low quality of BPL.

SUMMARY OF THE INVENTION

As a result of intensive research to overcome the above-mentioned problems, the present inventors have found that the debutylation rates of the four butyl groups in TBBPL are not egual, and that the rate slows as the number of butyl groups decreases. Therefore, the heat input required for the first debutylation reaction is fairly different than that for the last one. Accordingly, continuous debutylation of TBBPL using reactors separated to two or more steps in series can produce BPL with a high yield and high purity continuously on an industrial level.

The present invention is a method for preparing 4,4'-biphenol through debutylation of 3,3',5,5'-tetra-tert-butyl-4,4'-biphenol in an organic solvent in the presence of an acid catalyst wherein the debutylation is carried out continuously using at least two reactors aligned in series.

The addition of portions of the acid catalyst to each step increases the yield and purity.

Accordingly, an object of the present invention is to provide a method for preparing BPL, in which debutylation of TBBPL in two or more separate reactors is carried out by adding portions of an acid catalyst to each reactor, with a high yield and high purity on an industrial level.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram showing one of the methods according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Materials:

The TBBPL used in the present invention can be obtained by the oxidative dimerization of 2,6-DTBP, but the preparation method thereof is not limited.

TBBPL is usually continuously fed to the reactor in solution. Since the debutylation is an endothermic reaction, the raw materials are preferably preheated up to near the reaction temperature before being fed to the reactor.

Catalysts:

The method of the present invention uses an acid catalyst as a debutylation catalyst. Examples of the acid catalyst include sulfonic acids such as p-toluenesulfonic acid and sulfuric acid; and Lewis acids such as aluminum chloride, iron chloride and aluminum phenoxide.

The amount of the acid catalyst used is 0.1-20% by weight relative to the amount of the raw material TBBPL, and preferably 0.5-5% by weight.

In the method of the present invention, an acid catalyst is added continuously, and preferably added in portions to each reactor. The ratio of the portions is not limited, and thus an equal amount of acid catalyst may be added to each reactor. When the acid catalyst is added by such method, the catalyst concentration becomes higher in the down stream side than in the upper stream side in the series of reactor, to improve the yield and quality of the products.

Further, adding the catalyst as a solution of lower aliphatic alcohol such as methanol and the like or water rather than adding the catalyst itself is preferable for producing BPL with a high yield and high purity. It is deduced that such effects are attained by better catalyst dispersion and isobutene elimination. It is also possible to mix the catalyst with TBBPL solution before it is fed to the reactor.

Solvents:

The method of the present invention uses organic solvents in the debutylation reaction. The kind of such solvent is not intended to be limited; however solvents which meet the following requirements are preferably used:

1. A boiling point of 100 °C or higher because the reaction should be carried out at a temperature of at least 100 °C or higher;
2. To dissolve the raw material TBBPL relatively well; and the like.

Examples of the solvents include substituted aromatic compounds such as chlorobenzene, toluene, xylene, ethylbenzene, isopropylbenzene, tert-butylbenzene, diethylbenzene, isopropylbenzene, di-isopropylbenzene, naphthalene and methylnaphthalene; paraffins such as decalin, undecalin and tridecalin; and paraffin mixtures such as gas oil and the like.

The amount of the solvent used is 0.5-10 parts by weight relative to the amount of TBBPL, and preferably 1-5 parts by weight.

Reaction Conditions:

The reaction can be carried out in the temperature range of 100-220 °C in each reactor, and preferably in the range of 130-200 °C. Lower temperatures than that increase the reaction time, while higher temperatures causes the product to deteriorate and color. Further, the reaction is carried out preferably with the reaction temperature increasing from reactor to reactor so that high quality BPL can be obtained with high yield.

The reaction can be carried out in a pressure range of 0.1-3 atm in each reactor, and preferably in the range of 0.7-1.5 atm.

Figure 1 is an example of a flow diagram in accordance with the present invention. TBBPL and diethylbenzene (herein after referred to as DEB) are fed to the raw material tank attached a stirring and heating apparatus to dissolve TBBPL in DEB to prepare the feed solution.

The debutylation reaction is continuously carried out in reactor 1 and reactor 2 which are supplied enough heat for the endothermic debutylation reaction in each reactor. Vaporized DEB and the like are trapped by an overhead condensor and vessel, and isobutene which is generated by the butylation is not substantially condensed and vented away through a vent connected to the vessel.

Reaction product is continuously drawn out from the bottom of reactor 2.

In the method of the present invention, the debutylation of TBBPL is carried out continuously using two or more reactors aligned in tandem, and preferably from an economic and reaction-controlling point of view, carried out using two to five reactors.

In terms of detention time of the reaction mixture in the reactors, a total detention time of 1-15 hours in any reactor is suitable and about 2-10 hours is preferable. The detention time in each reactor is set depending on selection of the conversion rate in each step; thus it is preferable that the detention time in downstream reactors be set relatively shorter to achieve good yield and quality.

EXAMPLES

The method of the present invention will be illustrated with reference to the following examples, but the invention is not intended to be limited only to these following examples.

Example 1

Stirring type of reactors 1 and 2 (each having a volume of 5 L) with jackets were connected as shown in Fig. 1. A solution of TBBPL in diethylbenzene (DEB) and a solution of ptuluenesulfonic acid (PTSA) in methanol (MeOH) were fed to each reactor continuously under the conditions shown in Table 1 to cause debutylation. The effluent stream of reactor 2 was cooled down continuously to room temperature, and the precipitated BPL was separated from the solution using a centrifugal separator. The resultant precipitate was rinsed with pure water, and dried using a vacuum dryer to obtain white BPL with a yield of 86%.

This product was analyzed using a gas chromatograph and found to be 99.99% pure. Further, a 5% solution of the obtained crystal in methanol was evaluated for hue by measuring absorbance with a Shimazu UV-2100 spectrophotometer at 400 nm. Measured in a quartz cell 10 nm thick, the product had an absorbance of 0.042.

Example 2

Using three reactors, i.e. the two reactors in Example 1 plus one reactor as one step (not shown in the Figure), the debutylation was continuously carried out under the conditions shown in Table 1 as in Example 1.

Reactor output solution was continuously cooled down to room temperature, and the precipitated BPL was separated from the solution using a centrifugal separator. The resultant precipitate was rinsed with pure water, and dried using a vacuum dryer to obtain white BPL with a yield of 90%.

This product was analyzed using a gas chromatograph and found to be 99.99% pure. Further, a 5% solution of the obtained crystal in methanol showed an absorbance of 0.035.

Comparative Example 1

Using only a single reactor instead of the two reactors used in Example 1, the debutylation was carried out under the conditions are shown in Table 1 to obtain pink BPL with a yield of 73%.

This product was analyzed using a gas chromatograph and found to be 99.87% pure. Further, a 5% solution of the obtained crystal in methanol showed an absorbance of 0.228.

Example 3

Using three reactors in series as in Example 2, the debutylation was carried out. However, all catalyst was fed to the first reactor alone. Reaction conditions are shown in Table 1, and pale violet BPL was obtained with a yield of 81%.

This product was analyzed using a gas chromatograph and found to be 99.87% pure. Further, a 5% solution of the obtained crystal in methanol showed an absorbance of 0.186.

Examples 4 and 5

Using three reactors in series as in Example 2, the debutylation was carried out under the conditions shown in Table 2. The results are also summarized in Table 2.

Table 1: Reaction Conditions of Debutylation

Conditions	Example 1	Example 2	Comparative Example 1	Example 3
feed rate * of TBBPL:DEB (g/hr)	900	900	900	900
feed rate ** of PTSA:MeOH (g/hr)				
1st step	9.0	6.0	18.0	18.0
2nd step	9.0	6.0		0
3rd step		6.0		0
reaction temperature (℃)				
1st step	180	180	180	180
2nd step	180	180		180
3rd step	180	180		180
detention time (hr)				
1st step	2.25	1.5	4.5	1.5
2nd step	2.25	1.5		1.5
3rd step		1.5		1.5

*) TBBPL:DEB (weight ratio) = 1:1.25

**) PTSA:MeOH (weight ratio) = 2:1

Table 2: Reaction Conditions and Results of Debutylation

Conditions	Example 4	Example 5
feed rate * of TBBPL:DEB (g/hr)	900	900
feed rate ** of PTSA:MeOH (g/hr)		
1st step	6.0	4.5
2nd step	6.0	6.0
3rd step	6.0	7.5
reaction temperature (℃)		
1st step	170	170
2nd step	180	180
3rd step	190	190
detention time (hr)		
1st step	1.5	1.5
2nd step	1.5	1.5
3rd step	1.5	1.5
yield of BPL (%)	92	91
purity of BPL (%)	99.99	99.99
hue of BPL	0.029	0.024

*) TBBPL:DEB (weight ratio) = 1:1.25

**) PTSA:MeOH (weight ratio) = 2:1

Claims

1. A method for preparing 4,4'-biphenol through debutylation of 3,3',5,5'-tetra-tert-butyl-4,4'-biphenol in an organic solvent in the presence of an acid catalyst wherein said debutylation is carried out continuously

using at least two reactors aligned in series.

2. The method as claimed in claim 1 wherein two to five reactors are used.

3. The method as claimed in claim 1 or 2 wherein said acid catalyst is a Lewis acid selected from the group consisting of p-toluenesulfonic acid, sulfuric acid, aluminum chloride and iron chloride.

4. The method as claimed in any one of claims 1 to 3 wherein the amount of the acid catalyst used is 0.1-20% by weight relative to the amount of 3,3',5,5'-tetra-tert-butyl-4,4'-biphenol.

5. The method as claimed in any one of claims 1 to 4 wherein portions of said acid catalyst are added to each reactor.

6. The method as claimed in claim 5 wherein the acid catalyst concentration is increased from reactor to reactor along the series of reactors.

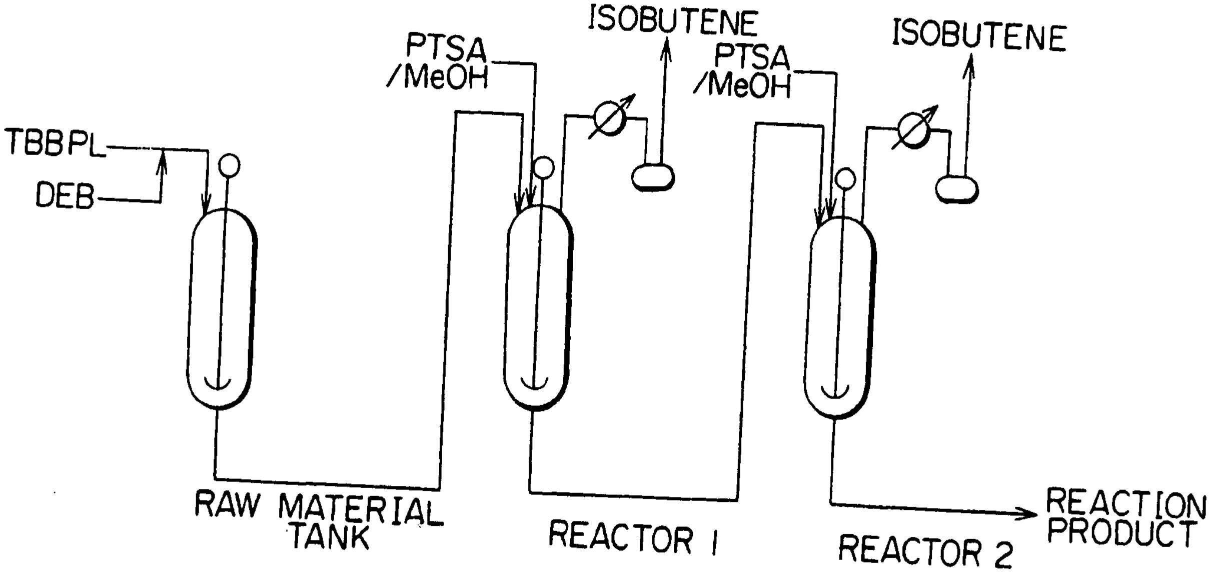
7. The method as claimed in any one of claims 1 to 6 wherein said reaction is carried out at a temperature range of 100-220 ° C.

8. The method as claimed in claim 7 wherein the reaction temperature is elevated from reactor to reactor along the series of reactors.

9. The method as claimed in claims 1 to 8 wherein the total detention time of the reaction mixture in all reactors is 1 to 15 hours.

10. The method as claimed in claim 9 wherein said detention time of each reactor is reduced from reactor to reactor along the series of reactors.

FIG . 1



TBBPL---3,3',5,5'-TETRA-tert-BUTYL BIPHENOL
DEB-----DIETHYLBENZENE
PTSA----p-TOLUENESULFONIC ACID
MeOH----METHANOL

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 8422

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CHEMICAL ABSTRACTS, vol. 110, no. 25, 19 June 1989, Columbus, Ohio, US; abstract no. 23172w, page 606 ;column 1 ; * abstract * & JP-A-63 301 837 (MITSUBISHI PETROCHEMICAL CO.) ---	1-10	C07C37/50 C07C39/15
A	CHEMICAL ABSTRACTS, vol. 117, no. 2, 13 July 1992, Columbus, Ohio, US; abstract no. 8669e, page 8679 ;column 1 ; * abstract * & JP-A-4 041 507 (DAINIPPON INK AND CHEMICALS) 31 January 1992 -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 JULY 1993	HEYWOOD C.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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XP-002274020

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FS - CPI
IC - B01J27/02 ; B01J31/02 ; C07B61/00 ; C07C37/48 ; C07C37/50 ; C07C39/15
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MC - A01-E13 E10-E02A N05-E02
M3 - [01] G013 G019 G100 H4 H402 H442 H8 M1 M111 M280 M320 M414 M510 M520 M532 M540 M720 M903 M904 N203 N209 N212 N221 N309 N321 N442 N513 N514 Q110; R06529-P; 1327-U 0502-U
- [02] G013 G100 K0 K4 K431 M210 M211 M240 M281 M320 M414 M510 M520 M531 M540 M730 M903 M910 Q421; 1327-U 0502-U
PA - (HONU) HONSHU CHEM IND CO LTD
PN - JP2169530 A 19900629 DW199032 000pp
- JP2582881B2 B2 19970219 DW199712 C07C39/15 004pp
PR - JP19880322762 19881221
XA - C1990-105165
XIC - B01J-027/02 ; B01J-031/02 ; C07B-061/00 ; C07C-037/48 ; C07C-037/50 ; C07C-039/15
AB - J02169530 Debutylating of 3,3',5,5'-tetra-tert- butyl-4,4'-biphenol (I) comprises (1) heating (I) in phenol (II) opt. 1-4C alkyl gp. having phenol to 130-250 deg. C in presence of debutylating catalyst (III) with removing isobutylene (IV), (2) recovering (IV) completely, (3) adding phenol or cresol to residue, and, (4) heating resulting mixt. to 180-220 deg. C to remove remaining tert-butyl gp. by transalkylation.
- Pref. (I) is heated in 0.1-1 (0.2-0.5) wt-fold (II) to 130-250 deg. C (pref. 150-220 deg. C) in presence of 0.01-5 wt.% (pref. 0.1-0.5 wt.%) (III) (opt. p-toluenesulphonic acid) for 5-6 hr. with removal of (IV). 25-150 (pref. 30-50) molar phenol and/or cresol per one remaining butyl gp. is added to the reaction mixt. The mixt. is heated to 180-200 deg. C for 1-4 hr. to complete transalkylation. The resulting matter is cooled, ppt. is filtered to obtain high purity (99.9%) (I) in 96% yield.
- USE/ADVANTAGE - 4,4'-Biphenol is useful as material for engineering plastics. (I) is debutylated under mild conditions and (IV) is recovered to use repeatedly. High purity (I) is prepd. more economically than prior art.
- (Dwg.0/0)
CN - R06529-P
DRL - 1327-U 0502-U
IW - HIGH PURE BI PHENOL PREPARATION COMPRISE TWO STEP DEBUTYLATION TETRA TERT BUTYL BI PHENOL USEFUL ENGINEERING PLASTICS
IKW - HIGH PURE BI PHENOL PREPARATION COMPRISE TWO STEP DEBUTYLATION TETRA TERT BUTYL BI PHENOL USEFUL ENGINEERING PLASTICS

NC - 001
OPD - 1988-12-21
ORD - 1990-06-29
PAW - (HONU) HONSHU CHEM IND CO LTD
TI - High purity 4,4-bi:phenol prepn. - comprises two steps debutylation of 3,3,5,5-tetra-tert-butyl-4,4-bi:phenol, useful for engineering plastics